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A Software System for Emission Spectrometry

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A SOFTWARE SYSTEM FOR EMISSION SPECTROMETRY

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ABSTRACT

A computer system was developed for an emission spectrometry facility consisting of a direct current (DC) argon arc spectrograph optically coupled to an inductively coupled plasma (ICP) multichannel spectrometer. Custom hardware and software were designed to control analytical functions and perform data acquisition. The software system was designed to make operation of the facility simple for routine operation and flexible for research and development.

Special software was written to collect data under controlled conditions to characterize and monitor system response. One sequence collects intensity versus time data on all channels and displays the data graphically. These profiles are useful in studying the effects of operating parameters on measurement precision. Another special sequence performs calibration using a spline curve fit procedure. Routines were also written to measure dark currents and signals from a standard tungsten halogen lamp mounted in place of the DC arc. For quality control purposes, histories of these values are kept and monitored for excess scatter or drift.

INTRODUCTION

An emission spectrometry facility consisting of a DC-argon arc spectrograph optically coupled to an ICP-multichannel spectrometer has been assembled at NASA Lewis Research Center. A customized hardware interface was designed to enable data acquisition and control of the analytical functions through a dedicated computer. Custom software was required to operate the interface and to collect and process experimental data. This report summarizes the design of the software system developed and highlights the special features which make operation of the system simple for routine operations and flexible for research and development.

EQUIPMENT

A block diagram of the instrumental components of the emission system is presented in figure 1. The components are grouped into four modules:

the computer, the DC arc-spectrograph, the ICP-spectrometer, and the hardware interface.

Computer

The computer is a Digital Equipment Corporation (DEC) PDP 11/23 with 256 kilobytes of memory. Peripherals include a VT-105 video terminal, dual RL01 disk drives, and a Texas Instruments 820-RO printer. Two DRV11 parallel input/output cards provide access to the interface module. Programs were written in FORTRAN IV, (DEC version 2.5), under RT-11, (DEC version 4.0). Other software development tools included a group of FORTRAN spline curve fitting routines called FITLOS (ref. 1), and DEC's FMS-11 form driver package.

Spectrometer

The spectrometer is a Jarrell Ash Model 750 Atomcomp. A group of 41 element lines was selected that includes optimum arc lines and ICP lines to match the workload requirements of the laboratory. A preamplifier motherboard with slots for 48 preamplifier cards was built to fit in the optical chamber of the spectrometer.

DC arc-Spectrograph

A controlled atmosphere arc chamber (ref. 2) is associated with the 3.4 meter Ebert mount spectrograph. Computer control of the spectrographic system was accomplished through the addition of a board of control relays which are activated by the interface to sequence the arc functions. The sample chamber contains a rotating tray capable of holding up to 11 analyte-doped electrodes.

Interface

The interface module (ref. 3), built to fit in the electronics cabinet of the spectrometer, holds fifty-five printed circuit cards. Forty-eight of the cards are counters which integrate and digitize the preamplifier outputs of the spectrometer. The remaining cards provide control logic for the counter cards and process signals to be sent to the spectrograph module.

SOFTWARE DESIGN AND IMPLEMENTATION

The software was designed to provide utilities for all desired functions of an emission spectrometry facility including several functions necessary for a research environment. Several guidelines were used in preparing the specifications. First, the emission system was to be useable by individuals with no "computer expertise." User-oriented prompts and help features were to be available at each decision point. Second, routine analyses were to require as few terminal keystrokes as possible; however, maximum flexibility in operating parameters had to be available for the nonroutine samples encountered in a research environment. Third, the software was to be written in modular form. By limiting programs and subroutines to manageable size, initial implementation was easier to debug, and later modifications are more straightforward.

The use of the FMS-11 forms driver package simplified implementation of the first two guidelines. The package provides routines to create video screens with defined input/output fields, and a library of subroutines to manipulate data to and from these fields. Two levels of help messages are available for use by the form designer: a one-line message specific to a field, and an entire screen corresponding to each form. In the emission system software, all entries on the forms are initialized with the most frequently used values as defaults. Therefore, the user simply types the RETURN key for routine operation which signifies that the default conditions are acceptable. For a non-routine application, the user advances the cursor to the necessary fields using the TAB key, and modifies those values. This method eliminates the tedious process of repeated keyboard entries. A further benefit of the forms package is that default values are stored with the form. Changing the defaults requires editing of the form only, not recompiling programs.

System Organization

A monitor program, MENU, was written to allow execution of the emission routines without knowledge of the operating system command language. This monitor presents a form indexing the available system activities, as shown in figure 2. The names of the corresponding executable files are stored in a table with the form. In order to initiate a task, the user simply enters that number in response to the 'Task?' prompt. The monitor then assembles an RT-11 command string from the appropriate file name and the proper routine is entered. the MENU program is automatically run at system start-up and is reentered at the conclusion of all emission system tasks. All normal system activities are accessible through MENU. Interaction with RT-11 is necessary only for program development activities.

The routines written for operation of the emission system can be grouped into four types of activities as shown in figure 3. These are system characterization, sample analysis, file maintenance, and troubleshooting. A fifth group of initialization routines were written to create system data files during system definition and are not accessible through MENU.

System characterization routines. - The flow diagram for the system characterization routines is shown in figure 4. These routines are a group of tasks which collect data under controlled conditions for the purpose of characterizing or monitoring system response.

The SETPRO-GETPRO-SHOPRO sequence is used to get intensity versus time profiles during an arc burn for standards of known element composition. This sequence was used extensively in the first phase of system installation to establish optimum operating parameters for the DC arc. Parameters under software control include the amount of current supplied to the arc, total arc burn time, chamber pump-down times, and signal integration times, which may be varied independently on each channel. Program SETPRO is used to initiate the profiling sequence. This program allows the user to specify the sequence and composition of standards to be analyzed. Program GETPRO then sequences the operation of the arc and collects data as a function of time on each channel. Program SHOPRO displays the resulting profiles graphically in several different modes for comparison purposes. For

example, the profiles for three replicates of a standard on one channel are shown in figure 5. These profiles are helpful in studying the effects of different current levels on measurement precision in order to arrive at the optimum current program. An additional feature of the display routine allows the summation of areas under the plots using variable endpoints. This feature can be used to determine start and stop times for signal integration to optimize the signal-to-noise ratio on each channel.

Calibration data are collected using the SETCAL-GETCAL-CALFIL sequence. SETCAL provides interactive dialog to define a calibration run. GETCAL performs data acquisition, and CALFIL stores the results of the run in special calibration data files. Program PROCAL is a set of modules which process the calibration data. Figure 6 shows one of the help forms available to the user during program execution. The raw data may be printed or tabulated on the screen and individual data points rejected. The FITLOS curve fitting package incorporated into PROCAL performs a spline fit of either a cubic or a quadratic polynomial in up to three splines. Log transforms of the data can be used. The results of the most recent curve fit may be printed or displayed on the screen graphically or in tabular form. When a satisfactory fit of the data is found, the results are stored in a coefficient file to be used by the sample analysis routines. Complete system calibration involves fitting calibration curves for each element on its detector and interference curves for those elements which cause significant response at other detectors. Recalibration of any element can be done without disturbing previous calibration data.

The last type of characterization routine provides for system quality control. The signal produced at each detector in response to a standard tungsten halogen lamp mounted in place of the DC arc is monitored. Program GETCTR begins by acquiring dark current data. Then current is supplied to the lamp and the lamp response is measured. Next, program PROCTR calculates gain factors for each channel by dividing the net lamp response into the day 0 lamp response for that channel. These gain factors are used to correct for shifts in system response. To minimize the effects of random variations, the values are compared with sets of values from the previous twenty runs. The most recent values are weighted with the historical averages. During this procedure, the historical data sets are monitored. Any excessive scatter or drift on a channel is detected and reported to the system console.

Sample analysis routines. - The analytical routines provide two methods of analyzing unknown samples. The first method performs a direct solution for all elements present by resolving spectral line interferences. The second is the analysis for trace constituents by the method-of-additions. The program flow diagram for the analysis routines is shown in figure 7. All of the analytical procedures begin with program GETRAY, in which the user specifies information about the run through interactive dialog. This information includes the sequence of standards and samples to be analyzed, composition of standards, the name of the file containing the operating parameters for the run, and descriptive information to be printed on sample reports. Different default set-ups are used in GETRAY depending on the task number chosen in MENU. A disk file designed to store all the data from the work session is created. Next, program GETDAT is initiated to control the sequence of events involved in igniting and sustaining the DC arc and to collect data on all channels. At the conclusion of the run, the data is

written to the disk file and program RSTFIL is entered. This program presents raw data in tabular form for operator review to allow rejection of data for any electrode that may have malfunctioned and then stores the result file permanently. At this point, one of two pathways is followed depending on the method chosen in MENU.

For the solution of concentrations using prestored calibration curves, program DPMENU is entered. It allows the user to choose which of the intermediate and final reports should be displayed or printed during the solution process. Then program RAPUD is executed. The raw data are corrected by averaging the replicates, subtracting the appropriate blanks, and multiplying by the current system gain factors. Next, the corrected channel signals are used along with the system calibration curves to solve for element concentrations in the sample. Figure 8 presents the flow diagram for the solution procedure. Initial concentration estimates are made by multiplying the corrected signal for each channel by a "first guess" factor for that channel. Then a loop is entered to iteratively calculate corrections to the estimates until the solutions converge. First, the expected signal at each detector is calculated from the calibration curves and the concentration estimates. Then the differences in the expected and observed signals are computed. A set of simultaneous equations is generated in which the derivatives of the calibration curves evaluated at the concentration estimates are multiplied by the corrections to the estimates and summed over all elements to yield the differences in the expected and observed signals. The equations are solved for the corrections using the Gauss-Jordan matrix reduction technique (ref. 4), and the corrections are added to the estimates to yield the next set of estimates. When the corrections all fall below a user-specified set of tolerances, the solutions have converged and any requested reports for the sample are printed.

For a method-of-additions analysis, program STMENU is entered from RSTFIL and the desired reports are selected. Then program STDADD fits the data for each element present in the standards to both a linear and a quadratic model and derives residual concentrations. The resulting curve fits may be displayed graphically for review.

File maintenance routines. - The flow diagram for the file maintenance routines is shown in figure 9. These routines perform edit or display functions for the system data files. Program PARFIL allows editing of existing arc operating parameter files or creation of new parameter files. Program PROBRN allows editing of the operating parameters used in the emission profiling sequence, and program CALPAR is used to modify the parameters and factors used in the solution process for the direct method of analysis. Each of the programs works by presenting the existing values in the file on specially designed video forms. The user advances the cursor to the value to be changed and replaces it with the new value. At the conclusion of the session, the file is rewritten with the new information.

Program HSTFIL may be used to inspect the data in the historical data file. The data can be displayed graphically or in tabular form.

Diagnostic routines. - The diagnostic routines, shown outlined in figure 10, were written to investigate system functions in the event of performance degradation. Program METER continuously monitors and displays the

output of a single detector for a variable integration time. Replicate values for all channels can be measured for variable time periods by the program COLLCT and printed along with the averages and standard deviations. Program MANUAL is used to manipulate the valves and switches of the arc chamber. It displays the current state of the functions on the system console.

CONCLUDING REMARKS

The use of this software design has simplified operation of the spectrograph-spectrometer system and has facilitated many of the research and development functions as well. Method development can be accomplished by first using the system characterization routines to study the effects of different operating parameters on an analysis and then creating a permanent file of those parameters found to be optimum. The calibration routine sequence resulted in a substantial decrease in the effort involved both in collecting calibration data and in generating curves. The effectiveness of the use of the standard lamp for quality control purposes will require evaluation over a long period of time.

REFERENCES

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3. Megargle, R. G.; and Gordon, W. A.: A New Data System for Emission Spectrometry. Presented at the Pittsburgh Conference on Analytical Chemistry and Applied Spectroscopy, (Atlantic City, NJ), Mar. 9-13, 1981, paper no. 526.
4. McCracken, D. D.; and Dorn, W. S.: Numerical Methods and FORTRAN Programming. John Wiley and Sons, Inc., 1964, pp. 226-283.

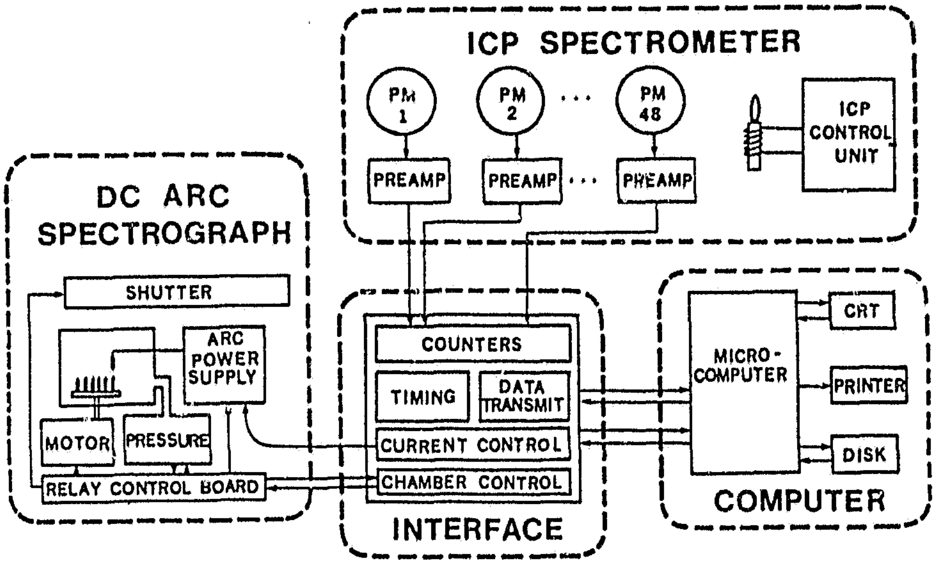

Figure 1. - Instrumental components of the emission system.

[1] GO TO RT-11	[9] FIT CALIBRATION CURVE	[17] EDIT RUN PARAMETER FILE
[2] RESTART SYSTEM	[10] REPROCESS RESULT FILE	[18] EDIT CALCULATION PARAMETERS
[3] RUN METHOD OF ADDNS	[11] MANUAL OPERATION	[19] EDIT PROFILE PARAMETERS
[4] RUN SPECIAL - RAPUD	[12] COLL EMISSION PROFILE	[20] RUN STANDARD LAMP-NO UPDAT
[5] [illegible] 1 SAMPLE - RAPUD	[13] COLL REPLICATE DATA	[21] EXAMINE HISTORY FILE
[6] RUN 2 SAMPLES - RAPUD	[14] DISPLAY EMISSION PROFILE	[22] RUN ICP METER AND AVG
[7] RUN STANDARD LAMP	[15] METER SINGLE CHANNEL	[23]
[8] RUN CALIBRATION STANDARD	[16] RUN SPECTROGRAPH ONLY	[24]

TASK?-

Figure 2. - The MENU form.

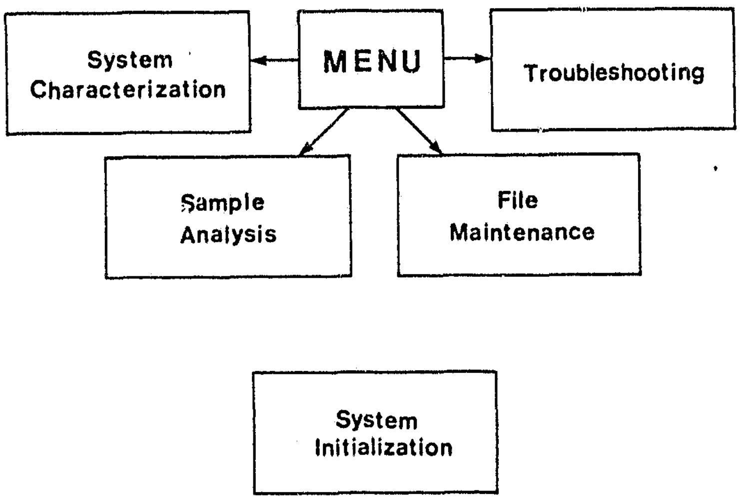

Figure 3. - Software overview.

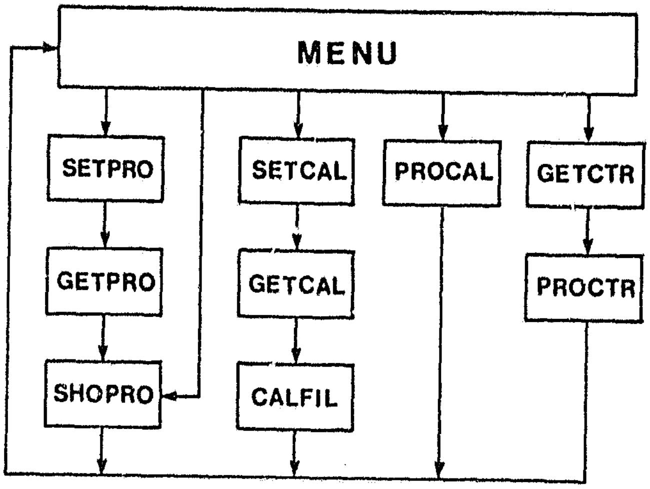

Figure 4. - System characterization routines.

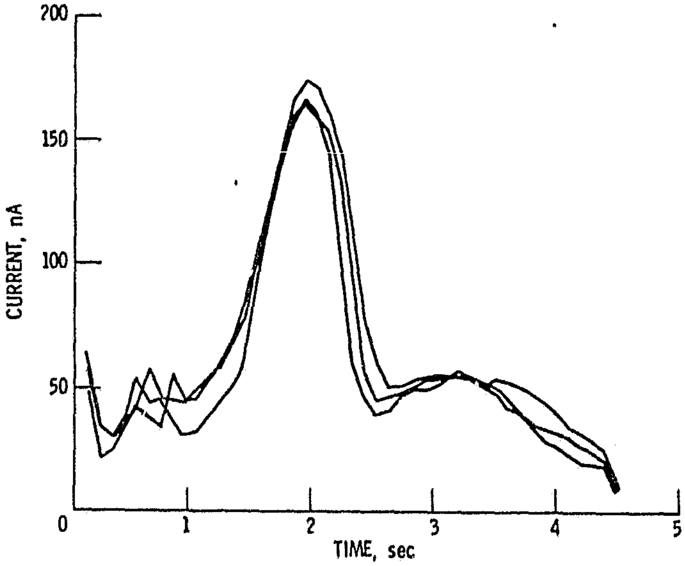

Figure 5. - Element emission profile.

OPTIONS AVAILABLE FOR THE PRESENT ELEMENT/CHANNEL COMBINATION:

- FT PERFORM CURVE FIT.
- PL DISPLAY THE FIT IN GRAPHICS MODE.
- TR DISPLAY THE FIT RESULTS IN TABULAR FORM ON THE SCREEN.
- TD DISPLAY THE DATA IN TABULAR FORM ON THE SCREEN.
- PR PRINT THE FIT RESULTS IN TABULAR FORM.
- PD PRINT THE DATA IN TABULAR FORM.
- AC STORE THE CURVE FIT COEFFICIENTS PERMANENTLY. (REMEMBER, THIS WILL DESTROY ANY PREVIOUSLY STORED CURVES FOR THIS PAIR).

OPTIONS TO CONTINUE:

- NX SELECT NEW ELEMENT/CHANNEL COMBINATION.
- EX END THE CURVE FITTING SESSION AND RETURN TO MENU.

Figure 6. - Help screen for program PROCAL.

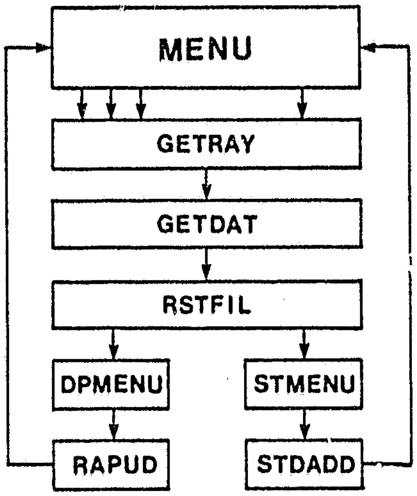

Figure 7. - Sample analysis routines.

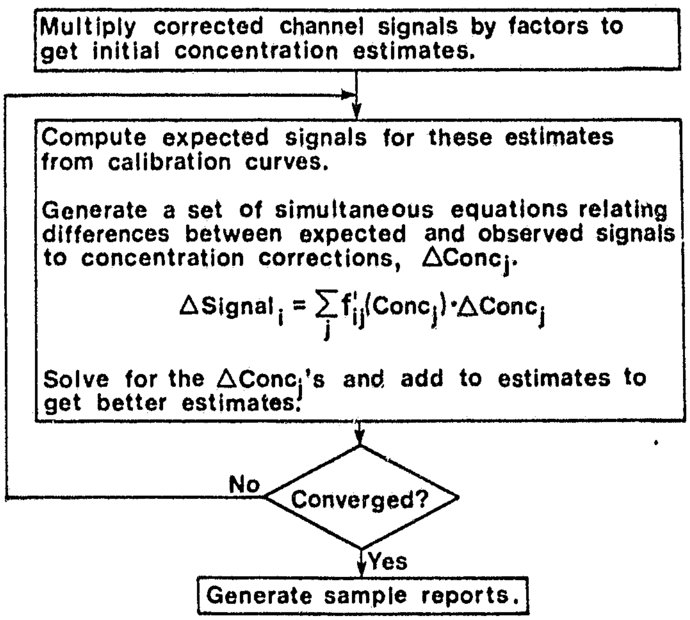

Figure 8. - Flow diagram for the direct solution process.

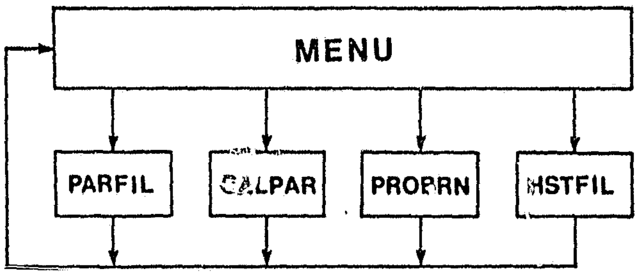

Figure 9. - File maintenance routines.

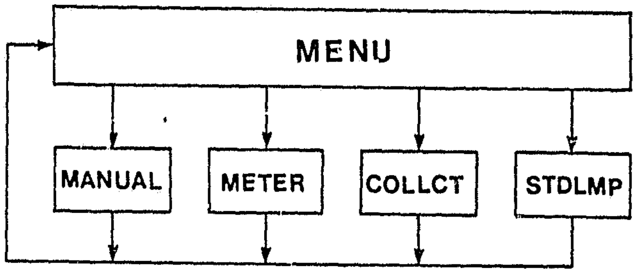

Figure 10. - Diagnostic routines.